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CITATION:

Katasho, Yumi ...[et al]. In situ synchrotron X-ray diffraction study of the electrochemical reduction of SiO in molten CaCl. *Electrochemistry Communications* 2020, 115: 106740.

ISSUE DATE:

2020-06

URL:

<http://hdl.handle.net/2433/250846>

RIGHT:

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Contents lists available at ScienceDirect

# Electrochemistry Communications

journal homepage: [www.elsevier.com/locate/elecom](http://www.elsevier.com/locate/elecom)



## *In situ* synchrotron X-ray diffraction study of the electrochemical reduction of SiO<sub>2</sub> in molten CaCl<sub>2</sub>

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### ARTICLE INFO

#### Keywords:

Molten salt

*In situ* analysis

Energy-dispersive X-ray diffraction

SiO<sub>2</sub>

Electrochemical reduction

CaCl<sub>2</sub>

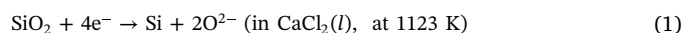
### ABSTRACT

*In situ* synchrotron X-ray diffraction was used to investigate the electrochemical reduction of SiO<sub>2</sub> to Si in molten CaCl<sub>2</sub> at 1123 K for the first time. The present technique enabled direct determination of intermediate products at high temperature, without cooling and washing treatments. Based on the diffraction data, the Ca<sub>2</sub>SiO<sub>4</sub> phase was detected inside the electrode, but not at the electrode edge. These results were explained by the presence of different concentrations of O<sup>2-</sup> ions in molten CaCl<sub>2</sub> permeating different regions of the electrode.

### 1. Introduction

Electrochemical reduction of SiO<sub>2</sub> in high-temperature molten salts has been attracting considerable attention as a new process for the production of high-purity silicon from SiO<sub>2</sub> [1–11]. This process has the potential to produce solar-grade silicon to replace the conventional (Siemens) process. Recently, electrochemical reduction of borosilicate glasses (whose main component is SiO<sub>2</sub>) has also been investigated for application in a new recovery process of long-lived fission products from vitrified wastes [12–14].

The electrochemical reaction mechanisms of insulating SiO<sub>2</sub> have been investigated for decades [1–11]. In these processes, molten CaCl<sub>2</sub>, which has high solubility of O<sup>2-</sup> ions, is typically used as an electrolyte. The direct contact of an electric conductor with SiO<sub>2</sub> in a molten salt enables the reduction of SiO<sub>2</sub> to Si by the following solid-state reaction:



The electrochemical reduction of SiO<sub>2</sub> starts at the conductor/in-sulator/electrolyte three-phase interphase [1,3,5]. Due to the high electric conductivity of Si at 1123 K, the reduction proceeds by creating a new three-phase interphase (SiO<sub>2</sub>/produced Si/CaCl<sub>2</sub>). Amorphous Si is first formed by electrochemical reduction and then thermally transformed to crystalline Si [3]. According to the thermodynamic

consideration using potential– $p\text{O}^{2-}$  diagrams, three solid calcium silicates, CaSiO<sub>3</sub>, Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>, and Ca<sub>2</sub>SiO<sub>4</sub>, were indicated as possible intermediates depending on the  $p\text{O}^{2-}$  value [6]. Among them, CaSiO<sub>3</sub> was suggested to be most likely one by *ex situ* X-ray photoelectron spectroscopy [6].

*In situ* synchrotron X-ray diffraction is a useful technique for phase identification. Most previous studies of the electrochemical reduction of oxides in molten salts have employed *ex situ* phase identification methods, after cooling and washing the reduction samples. However, the crystal structures of the samples might change during the cooling process, and the washing treatment might induce chemical reactions as well as the removal of water-soluble species. *In situ* synchrotron X-ray diffraction measurements were previously performed to identify the intermediate compounds in the electrochemical reduction of TiO<sub>2</sub> [15] and NiTiO<sub>3</sub> [16] in molten CaCl<sub>2</sub>, as well as of UO<sub>2</sub> [19] in molten LiCl–KCl. In the case of TiO<sub>2</sub>, sub-stoichiometric phases such as CaTiO<sub>3</sub> and CaO were reported as intermediate products during the reduction reaction [15]. In the reaction of NiTiO<sub>3</sub>, CaO was not detected and only CaTiO<sub>3</sub> was confirmed as an intermediate oxide product [16]. Moreover, no intermediate products were reported for the electrochemical reduction of UO<sub>2</sub> in molten LiCl–KCl [19]. In the present study, *in situ* synchrotron X-ray diffraction was employed to determine the phase

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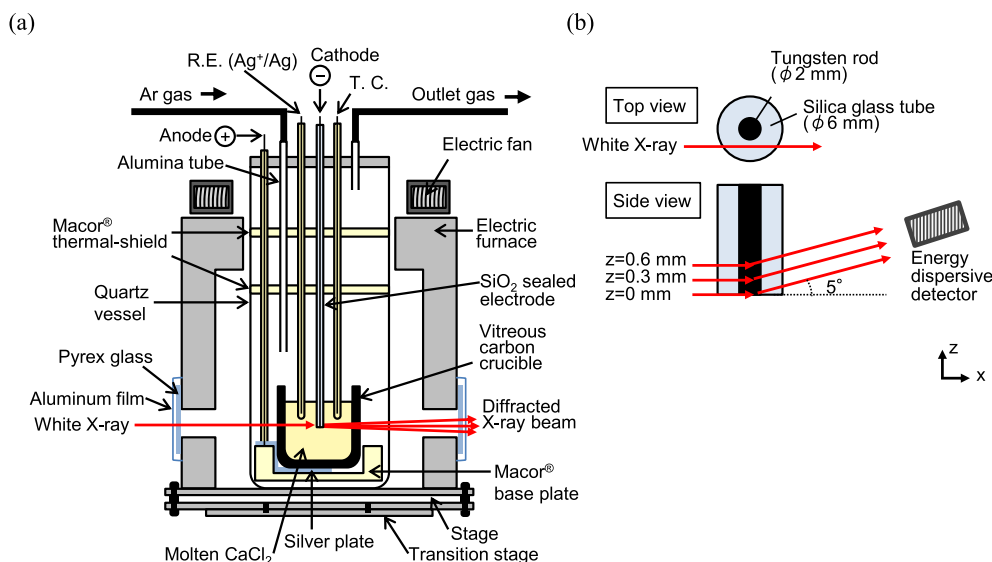
<https://doi.org/10.1016/j.elecom.2020.106740>

Received 7 March 2020; Received in revised form 2 May 2020; Accepted 4 May 2020

Available online 05 May 2020

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**Fig. 1.** (a) Schematic illustration of *in situ* experimental apparatus for electrochemical reduction of SiO<sub>2</sub> in molten CaCl<sub>2</sub> at 1123 K. (b) Scheme of glass-sealed electrode and beam path.

composition during the electrochemical reduction of SiO<sub>2</sub> in molten CaCl<sub>2</sub> and further investigate the corresponding reduction mechanism.

## 2. Experimental

Fig. 1a shows a schematic illustration of the experimental apparatus. Before the experiment, 25.0 g of CaCl<sub>2</sub> (> 95%, Fujifilm Wako Pure Chemical Co., Ltd.) was placed in a vitreous carbon crucible (outer diameter (o.d.) 40 mm, height 40 mm, purity 99%, Tokai Carbon Co., Ltd.) set in an open dry chamber (HRW-60AR, Daikin Co., Ltd.). The crucible containing CaCl<sub>2</sub> was successively dried at 453 K for 2 h, at 773 K for 12 h under vacuum, and at 1123 K in dry Ar atmosphere for 6 h. The experiment was carried out at the BL28B2 beamline of SPring-8 in Hyogo, Japan. A vertical electric furnace with four windows was designed to allow white X-rays to penetrate. The electrolysis was conducted inside a quartz glass vessel at 1123 K in a dry Ar atmosphere. To avoid heat damage, the windows were covered with aluminum films. The temperature was controlled by two chromel–alumel thermocouples; one was installed in the vertical furnace and the other was immersed in the molten salt.

Electrochemical measurements and electrolysis were conducted in a three-electrode configuration using an electrochemical measurement system (HZ-7000, Hokuto Denko Corp.). The vitreous carbon crucible and a silver plate (10 mm × 30 mm × 0.1 mm, 99.98%, Nilaco Corp.) were used as counter electrode and current lead, respectively. The reference electrode was an Ag<sup>+</sup>/Ag electrode prepared by immersing a silver wire (diameter 1.0 mm, 99%, Nilaco Corp.) in a CaCl<sub>2</sub> melt containing 0.5 mol% AgCl (99.5%, Fujifilm Wako Pure Chemical Co., Ltd.) placed in a mullite tube (o.d. 6 mm, inner diameter (i.d.) 4 mm, SiO<sub>2</sub> 40%, Al<sub>2</sub>O<sub>3</sub> 56%, Nikkato Corp.) [6]. The potentials were calibrated by the Ca deposition/dissolution potential measured by an Mo electrode (diameter 1.0 mm, > 99.95%, Nilaco Corp.) [6] before the start of the electrolysis of SiO<sub>2</sub>.

Fig. 1b shows a schematic illustration of the glass-sealed electrode and beam paths. The SiO<sub>2</sub> glass-sealed electrode, employed as working electrode, was prepared by inserting a tungsten rod (diameter 2.0 mm, > 99.95%, Nilaco Corp.) into a silica glass (amorphous SiO<sub>2</sub>) tube (o.d. 6.0 mm, i.d. 2.0 mm) [12]. Cyclic voltammetry (CV) measurements were performed immediately before the electrolysis (scan rate 100 mV s<sup>-1</sup>, 1 cycle, potential range 2.0–0.3 V vs. Ca<sup>2+</sup>/Ca). Using the same electrode employed for the CV measurements, the electrolysis was conducted by scanning the potential from the open circuit value to

0.7 V vs. Ca<sup>2+</sup>/Ca at a rate of 0.5 mV s<sup>-1</sup>, and then keeping the potential at 0.7 V for 150 min. The measurement of the white X-ray diffraction spectrum started at the same time as the potential scan. The size of the incident beam was 50 μm (height) × 200 μm (width) and the take-off angle was set at 2θ = 5°. The sizes of the two slits in front of the detector were 50 μm × 3 mm and 50 μm × 8 mm (height × width). The vertical electric furnace was set on the transition stage. The diffracted X-rays were consecutively detected at three different heights: the bottom edge of the electrode (z = 0 mm) and two points inside the electrode (z = 0.3 and 0.6 mm). The acquisition time for each pattern was 120 s. An energy-dispersive X-ray detector (Ge solid-state detector, GLP-16195/10P4, ORTEC) was employed in the range of 0–200 keV. The number of obtained data points was 4096 (data points for one spectrum) × 30 or 31 (times) × 3 (measured z positions). For each position, a spectrum was obtained with a time resolution of approximately 6 min. The spectra were analyzed in the range of 50–100 keV, which contained around 900 data points.

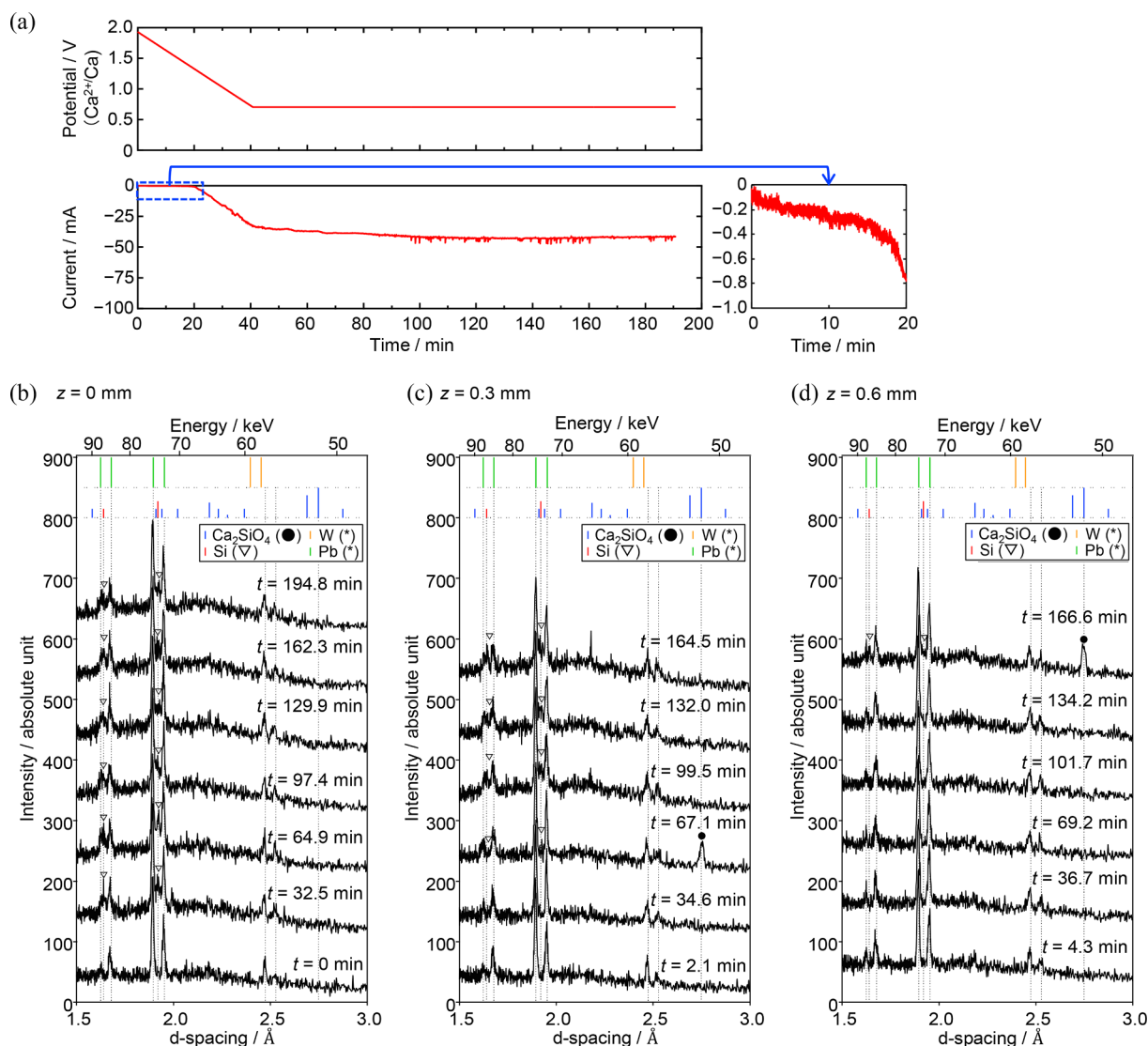
## 3. Results and discussion

Fig. 2 shows the potential–time (a) and current–time (b) curves during the electrolysis. During the potential scanning in the negative direction, the cathodic current starts flowing from ca. 20 min, corresponding to a potential of 1.3 V. After ca. 40 min, the potential remains stable at 0.7 V and the cathodic current around 40 mA lasts until the end of the electrolysis. Such trends agree with the reported starting potential of SiO<sub>2</sub> reduction and with the current values in potentiostatic electrolysis experiments using the same electrode [4,12]. After the experiment, the color of the edge of the SiO<sub>2</sub>-sealed electrode changes from colorless to brown, indicating the reduction of SiO<sub>2</sub> to Si.

Fig. 2b–d show the selected energy-dispersive X-ray diffraction (EDXRD) data at z = 0, 0.3, and 0.6 mm, respectively. The d-spacing values were calculated from the photon energy measured at the detector according to equation (2), derived from Bragg's law with a take-off angle of 2θ = 5°:

$$d(\text{\AA}) = \frac{12.40}{2 E \sin \theta (\text{keV})} \quad (2)$$

In addition to several peaks for Si [17] and α'-Ca<sub>2</sub>SiO<sub>4</sub> [18], the fluorescence peaks of Pb from the beamline instruments appear at 75.03 (Pb K<sub>α1</sub>), 72.76 (Pb K<sub>α2</sub>), 84.68 (Pb K<sub>β1</sub>), and 87.48 (Pb K<sub>β2</sub>) keV [20,21]. Hereafter, the high temperature α'-Ca<sub>2</sub>SiO<sub>4</sub> phase is simply



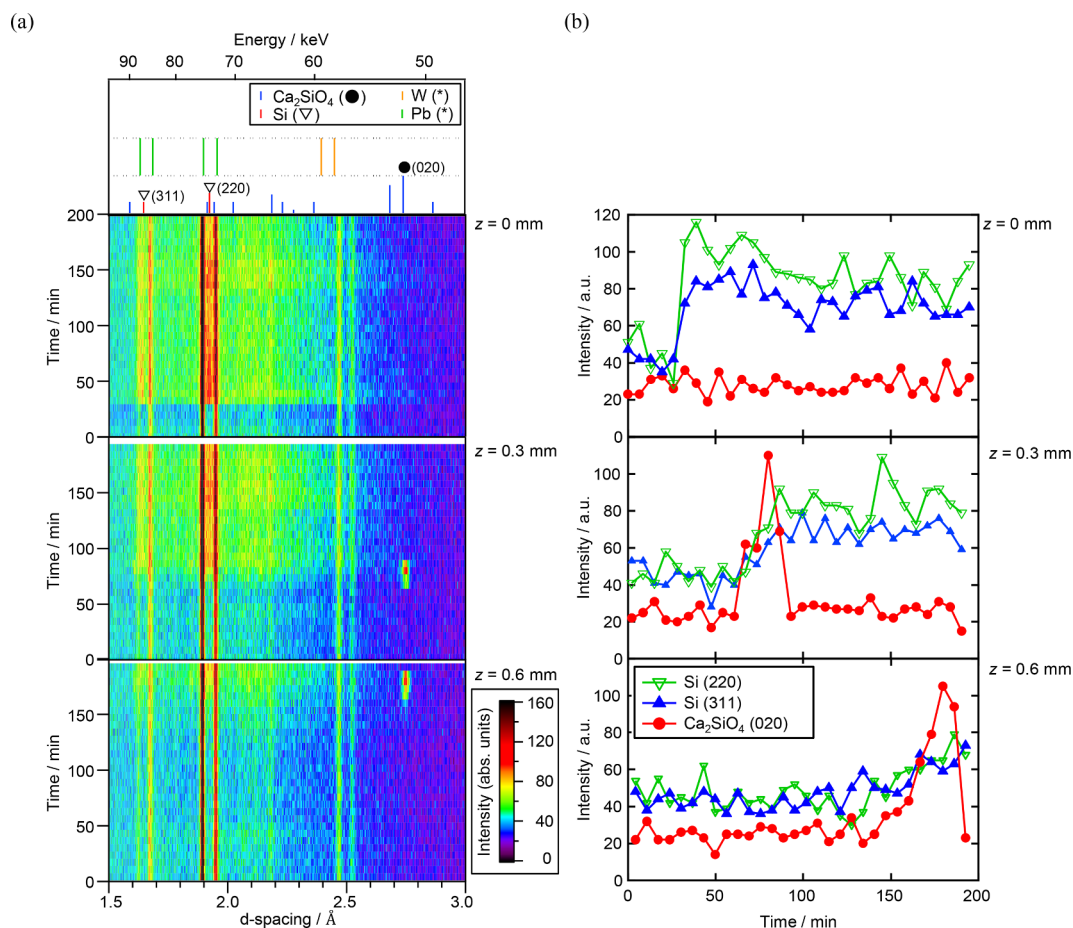
**Fig. 2.** (a) Potential–time (top) and current–time (bottom) curves during the experiment. (b) Selected raw EDXRD data at different times for (b)  $z = 0$  mm, (c)  $z = 0.3$  mm, and (d)  $z = 0.6$  mm. (\*) Peaks from X-ray fluorescence. The shifts of the W fluorescence peaks are due to the energy loss when X-ray is passing through the inside of the electrode.

denoted as Ca<sub>2</sub>SiO<sub>4</sub>. The peaks at 56.22 and 57.46 keV probably represent shifted W K<sub>α1</sub> and W K<sub>α2</sub> fluorescence signals, respectively, and can be attributed to the tungsten rod in the SiO<sub>2</sub>-sealed electrode. The shifts of the W fluorescent signals are explained by the energy loss when X-ray is passing through the inside of the electrode consisting of SiO<sub>2</sub>, produced Si and Ca<sub>2</sub>SiO<sub>4</sub>. The measured intensity is shown as raw EDXRD color map data as a function of time in Fig. 3a. A dark red color denotes high-intensity signals. Among the observed signals, the Ca<sub>2</sub>SiO<sub>4</sub> (0 2 0) ( $E = 51.75$  keV), Si (3 1 1) ( $E = 86.78$  keV), and Si (2 2 0) ( $E = 74.00$  keV) peaks were used for the evaluation and determination of the reaction products. Among several reported diffraction peaks for Ca<sub>2</sub>SiO<sub>4</sub>, only the (0 2 0) peak that is the strongest one for Ca<sub>2</sub>SiO<sub>4</sub> was observed, indicating that the produced Ca<sub>2</sub>SiO<sub>4</sub> had high orientation. Such high orientation might occur when the reaction proceeds in one direction. Incidentally, other possible solid compounds,  $\alpha$ -quartz,  $\beta$ -CaSiO<sub>3</sub>, Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>, CaO [21], did not match the peak at  $E = 51.75$  keV. The sharp peak at approximately 65 keV at 164.5 min at  $z = 0.3$  mm seems to be a background noise taking the width of the peak into account.

Fig. 3b shows the intensity–time curves of the Ca<sub>2</sub>SiO<sub>4</sub> (0 2 0), Si (3 1 1), and Si (2 2 0) peaks at each  $z$  position indicated in Fig. 3a. At

$z = 0$  mm, the formation of Si is observed after 25 min, which matches the time when the reduction current starts flowing at 1.3 V in Fig. 2a. On the other hand, Ca<sub>2</sub>SiO<sub>4</sub> is not detected at  $z = 0$  mm during the electrolysis. At  $z = 0.3$  mm, the Si (3 1 1) and Si (2 2 0) signals increase after 60 min. At the same time, the Ca<sub>2</sub>SiO<sub>4</sub> (0 2 0) signal also increases and then drops within 25 min. Similar trends, i.e., simultaneous signal increases for Si (3 1 1), Si (2 2 0), and Ca<sub>2</sub>SiO<sub>4</sub> (0 2 0), are observed after 150 min at  $z = 0.6$  mm. A different feature with respect to the trend observed for  $z = 0.3$  mm is that the Si (3 1 1) and Si (2 2 0) signals increase more gradually at  $z = 0.6$  mm, indicating that the reduction rate slows down going from the edge to the interior of the electrode. The 1-h reduction rate of SiO<sub>2</sub> observed in the present study (ca. 300  $\mu$ m for 1 h) is consistent with that reported in a previous study (approximately 200  $\mu$ m at 1.00 V and 400  $\mu$ m at 0.70 V in the initial 1 h) [4].

Herein, the edge ( $z = 0$  mm) and interior ( $z = 0.3$  and 0.6 mm) of the electrode exhibit different behaviors in terms of formation of Ca<sub>2</sub>SiO<sub>4</sub> and reduction rate of SiO<sub>2</sub>. These differences can be explained by the different diffusivity of O<sup>2-</sup> ions in molten CaCl<sub>2</sub> permeated into the electrode. Due to their low diffusivity inside the electrode, the electrochemically produced O<sup>2-</sup> ions tend to accumulate, which results



**Fig. 3.** (a) Color map from raw EDXRD data as a function of time for  $z = 0, 0.3$ , and  $0.6$  mm. (\*) Peaks from X-ray fluorescence (note: the reason for the shift of the W fluorescence peak is unclear). (b) Intensity–time curves for  $\text{Ca}_2\text{SiO}_4$  (0 2 0) ( $E = 51.75$  keV), Si (3 3 1) ( $E = 86.78$  keV), and Si (2 2 0) ( $E = 74.00$  keV) signals at each  $z$  position.

in slow electrochemical reduction *via* formation of the  $\text{Ca}_2\text{SiO}_4$  intermediate. On the other hand, since  $\text{O}^{2-}$  ions are easily removed from the edge of the electrode, fast electrochemical reduction without formation of  $\text{Ca}_2\text{SiO}_4$  occurs in this region. The potential– $\text{pO}_2$  diagram of the Ca–Si–O system [6,13] confirms the stability of calcium silicates in low  $\text{pO}_2$  (i.e., high  $\text{O}^{2-}$  ion concentration) regions.

The present study reveals both similar and different trends compared with previous *in situ* synchrotron X-ray diffraction studies of the electrochemical reduction of  $\text{TiO}_2$  [15] and  $\text{NiTiO}_3$  pellets [16]. It should be noted that the dense  $\text{SiO}_2$  electrode was used in the present experiment, and that  $\text{TiO}_2$  and  $\text{NiTiO}_3$  porous pellets were used in the previous researches. The similar trend is represented by the lower reduction rate inside the electrode, which applies to all three investigated cases ( $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{NiTiO}_3$ ). The different behavior concerns the lifetime of the intermediate phases. The lifetime of the  $\text{CaTiO}_3$  intermediate was more than 4 h for  $\text{TiO}_2$  and  $\text{NiTiO}_3$  even at the edge of the electrode, while in the case of  $\text{SiO}_2$ , the  $\text{Ca}_2\text{SiO}_4$  lifetime at the edge of the electrode was only around 25 min. The different lifetime is probably due to the different stability of the intermediates. Even though porous pellets were used in the previous studies of  $\text{TiO}_2$  and  $\text{NiTiO}_3$ , which is advantageous for fast diffusion of  $\text{O}^{2-}$  ions, the lifetime was much longer than that of the present system, involving dense  $\text{SiO}_2$ , which reflects the high stability of  $\text{CaTiO}_3$ . Moreover, the different electrode configurations (two- and three-electrode systems were used in the previous studies and the present one, respectively) might influence the electrochemical reduction behavior. Clearly, the three-electrode system is preferable for the precise control of the working electrode potential. Since much faster reduction rate was reported for  $\text{SiO}_2$  powders piled on a current collector (approximately 3 mm at

0.80 V and 4 mm at 0.60 V in the initial 1 h) [11], *in-situ* X-ray diffraction study is also needed for  $\text{SiO}_2$  porous pellets or powders.

#### 4. Conclusions

The electrochemical reduction of  $\text{SiO}_2$  to Si in molten  $\text{CaCl}_2$  at 1123 K was investigated by *in situ* synchrotron X-ray diffraction using a  $\text{SiO}_2$  sealed electrode. The  $\text{Ca}_2\text{SiO}_4$  phase was detected inside the electrode as an intermediate product formed during the electrochemical reduction of  $\text{SiO}_2$  to Si, whereas the same phase was not detected at the edge of the electrode. The difference in  $\text{Ca}_2\text{SiO}_4$  formation behavior can be explained by the occurrence of different  $\text{O}^{2-}$  ion concentrations at different locations. As the reduction proceeded, the  $\text{Ca}_2\text{SiO}_4$  phase disappeared in 25 min. Finally, the reduction rates of  $\text{SiO}_2$  were observed to decrease from the edge toward the interior of the electrode.

#### CRediT authorship contribution statement

**Yumi Katasho:** Conceptualization, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Funding acquisition. **Yutaro Norikawa:** Validation, Investigation, Resources, Writing - review & editing. **Takayuki Yamamoto:** Validation, Investigation, Resources, Writing - review & editing. **Kouji Yasuda:** Validation, Investigation, Resources, Writing - original draft, Writing - review & editing. **Toshiyuki Nohira:** Conceptualization, Validation, Investigation, Resources, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition.



## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

This work was supported by JSPS KAKENHI Grant Number 17J08901 and 16H02410. The synchrotron radiation experiments were performed at the BL28B2 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2017B1682). The authors thank Dr. Kentaro Kajiwaru at JASRI for his assistance on operating the beamline.

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